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MOLYBDENUM-INFILTRATED BIOGEOCHEMICAL PROVINCES

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V. V. Koval'skiy, G. A. Yarovaya

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V. V. Koval'skiy, C. A. Yarovaya

MOLYBDENUM-INFILTRATED BIOGEOCHEMICAL PROVINCES

Interest in the study of molybdenum-infiltrated biogeochemical provinces stems from a variety of reasons.

The data in the literature tell us that animals that feed on plants that have stored substantial quantities of molybdenum (as high as thousands of a percent and more in terms of dry weight) develop a specific disease that can be considered to be chronic molybdenum toxicosis. The symptoms of this disease, known as molybdenosis, are extremely severe diarrhea, loss of weight, change in color, coarsening of the wool, and subsequent falling out of the wool. Molybdenosis in sheep and in large-horned cattle has been observed in England [1, 2], the United States [3, 4], Canada [5], New Zealand [6, 7], and Sweden [8]. The physiological function performed by molybdenum in the animal organism was elucidated in 1953. It was found that molybdenum is an indispensible structural component of xanthine oxidase [9-12], the enzyme that catalyzes the formation of uric acid in the animal organism. This made it possible to raise the question of change in purine metabolism in animals and humans under the natural conditions that prevail in an environment with an elevated molybdenum content.

The molybdenum provinces within the USSR have not, as yet, been described.

At the basis of the theory of biogeochemical provinces, a theory that reflects the closest possible connection between living organisms

and the environment, is the concept of the migration of chemical elements within a soil-plant-animal organism system. This triad is a natural system, understanding of each part of which is impossible without the other links in the migration chain. For example, it is impossible to limit oneself simply to a determination of the chemical elements in the fodder consumed by animals, or to simply take into consideration the status of the metabolism of substances in the organism without taking into consideration the composition of the fodder. And there can be no answer to the question of the mineral composition of fodders without these latter being linked with the question of the content of minerals in the soil, because change in soil composition and properties is what regulates the storage of definite chemical elements in plants. This is why study of biogeochemical provinces is complex in nature.

We were faced with several tasks in studying molybdenum biogeochemical provinces.

1. Ascertain the biogeochemical characteristics of the environment, and of the organisms inhabiting the environment. Link the anomaly in the molybdenum content with the geochemical conditions prevailing in the province, and indicate the behavior pattern in the migration of this element under the given set of conditions.

2. Ascertain the reactions of living organisms to the prevailing molybdenum level. Make comparative geobotanical studies in territories with different molybdenum contents. Study changes in the purine metabolism

in the organisms of animals and humans in the case of an excess content of molybdenum in the environment.

3. Consider the influence of the associated element, copper in this particular case, on the molybdenum metabolism, because these two elements are closely linked in the metabolism of substances in the animal organism, being, as they are, antagonists.

4. Make comparative studies in neighboring areas not enriched with molybdenum, but similar to the molybdenum areas in natural conditions, for purposes of use as controls.

5. Map the biogeochemical provinces; that is, map their boundaries and plot the molybdenum concentration isolines.

We studied three regions in Armenia, Ankavan, Kadzharan, and Dastakert, all of which are located in high-mountain areas, the orographic habit of which is distinguished by its complexity and variegation. The Ankavan biogeochemical province is located in the central part of Armenia, and the basic structural element of the province is the north wing of the Miskhano-Arzakanskaya anticline. The Kadzharan and Dastakert provinces are located in the southeastern part of Armenia. These latter two regions are very similar in terms of the genetic type of their component rocks, and both are part of the broad Zangezurskaya metallogenetic province.

The rocks composing these regions are infiltrated by molybdenum. We know that molybdenum migrates from the parent rock oxidation zone into the soil horizons, forming dispersion halos and infiltrating the soils, waters, plants, and animal organisms.

The molybdenum in all objects studied was determined by the colorimetric thiocyanate method, using tin chloride as the reducing agent [13, 14]. The copper determination was by the colorimetric method using sodium diethyldithiocarbamate [15, 16].

Content and Migration of Molybdenum and Copper in Soils, Waters, and Plants in the Ankavan Biogeochemical Province

The study of the chemical features of this biogeochemical province, and its mapping, involved the collection and analysis for Mo and Cu content of 194 soil and rock samples, 45 water samples, and 326 plant specimens from 52 sites, for which botanical and soil reports were made. Tables 1 and 2 list the mean molybdenum and copper contents in the soils and plants infiltrated with molybdenum, as well as those in the control territory.

Molybdenum in the province's soils. According to Vinogradov [17], the content of molybdenum in the soils of the Soviet Union, and in the soils of certain other countries, is more or less the same for the different types of soils, and is a mean of 2.6×10^{-4} percent. The molybdenum content in the soils of the biogeochemical province studied exceeds this figure by a factor of 10-100.

Molybdenum predominates over copper in the soils of this province (Mo:Cu = 1.4:1), and in those sections in which the molybdenum concentration is high the percentage relationship between molybdenum and copper increases by a factor of from 3 to 5. And it is this fact that sets the Ankavan province well apart from neighboring regions outside the boundaries of the province, from other of the molybdenum provinces in Armenia, and from the chernozem zone, where copper prevails over molybdenum.

The sharp variations in the quantity of molybdenum at individual points in the soil cover can be explained by the nonuniform molybdenum infiltration of basement rocks and the dissimilar development of oxidation processes in the different rocks, as well as by the peculiarities in soil conditions that influence the migratory capacity of molybdenum.

Variations in molybdenum content in soils outside the province boundaries are slight, the result of a more uniform distribution of the mineral in the rock, and can only be attributed to soil conditions and the relief.

Little study has thus far been given to the behavior of molybdenum in soils, or to the forms of its compounds. We know that a relative surplus, or lack, of molybdenum, and the mobility of its compounds, depend on soil reactions [1, 17-19]. Alkaline soils, and soils rich in organic matter, contain a readily exchanged, mobile MoO_4^{-2} ion. Acid soils with a sharply pronounced podzol process fix the molybdenum in the inwash horizons where it becomes virtually immobilized and is not available to plants.

Analysis of the samples selected confirmed this behavior pattern. The mountain meadow soils of the Ankavan biogeochemical province (pH 5.2-7.6) contain more molybdenum than do the more acid brown mountain forest soils (pH 4.2-6.8). The deviations from this behavior pattern noted in a number of cases are related to the influence of other factors. The elevated content of molybdenum in the acid waterlogged soils in this same province (pH 4.0-5.3) can be explained by the fact that molybdenum readily forms complexes with the organic matter of soils, and can be absorbed quite well in all types of soil colloids [18-20].

Table 1

MEAN CONTENT OF MOLYBDENUM AND COPPER IN THE SOILS OF MOLYBDENUM BIOGEOCHEMICAL PROVINCES, IN % OF DRY MATERIAL*

Region	Type soil	Infiltrated Province			Control Region		
		Mo	Cu	Mo:Cu	Mo	Cu	Mo:Cu
Ankavan	Mountain meadow	$7.9 \cdot 10^{-3}$ ($9.7 \cdot 10^{-4}$ - $1.5 \cdot 10^{-2}$)	$4.9 \cdot 10^{-3}$ ($1.3 \cdot 10^{-3}$ - $1.1 \cdot 10^{-2}$)	1.6:1	$3.6 \cdot 10^{-4}$ ($9.5 \cdot 10^{-5}$ - $5.6 \cdot 10^{-4}$)	$3.1 \cdot 10^{-3}$ ($1.9 \cdot 10^{-3}$ - $5.4 \cdot 10^{-3}$)	1:8.6
	Brown mountain forest	$5.5 \cdot 10^{-3}$ ($8.6 \cdot 10^{-4}$ - $8.8 \cdot 10^{-3}$)	$5.4 \cdot 10^{-3}$ ($1.6 \cdot 10^{-3}$ - $1.2 \cdot 10^{-2}$	1:1	$2.2 \cdot 10^{-4}$ ($9.8 \cdot 10^{-5}$ - $3.3 \cdot 10^{-4}$)	$3.9 \cdot 10^{-3}$ ($2.1 \cdot 10^{-3}$ - $5.5 \cdot 10^{-3}$)	1:17.7
	Waterlogged	$6.3 \cdot 10^{-3}$ ($2.4 \cdot 10^{-3}$ - $1.0 \cdot 10^{-2}$)	$4.4 \cdot 10^{-3}$ ($2.0 \cdot 10^{-3}$ - $6.5 \cdot 10^{-3}$)	1.4:1	-- ($1.2 \cdot 10^{-4}$ - $4.6 \cdot 10^{-4}$)	-- ($1.7 \cdot 10^{-3}$ - $4.5 \cdot 10^{-3}$)	--
Mean for the province		$6.9 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	1.4:1	$3.1 \cdot 10^{-4}$	$3.4 \cdot 10^{-3}$	1:11.0
Kadzharan	Chestnut	$9.8 \cdot 10^{-3}$ ($4.4 \cdot 10^{-3}$ - $1.7 \cdot 10^{-2}$)	$9.1 \cdot 10^{-2}$ ($7.2 \cdot 10^{-2}$ - $1.3 \cdot 10^{-1}$)	1:9.3	$4.5 \cdot 10^{-4}$ ($1.9 \cdot 10^{-4}$ - $9.7 \cdot 10^{-4}$)	$4.8 \cdot 10^{-3}$ ($1.8 \cdot 10^{-3}$ - $6.9 \cdot 10^{-3}$)	1:10.7
	Gray mountain forest	$1.2 \cdot 10^{-2}$ ($3.6 \cdot 10^{-3}$ - $2.0 \cdot 10^{-2}$)	$1.5 \cdot 10^{-1}$ ($6.9 \cdot 10^{-2}$ - $2.4 \cdot 10^{-1}$)	1:12.5	--	--	--
Mean for the province		$1.1 \cdot 10^{-2}$	$1.2 \cdot 10^{-1}$	1:10.9	--	--	--

Table 2

MEAN CONTENT OF MOLYBDENUM AND COPPER IN THE PLANTS OF MOLYBDENUM BIOGEOCHEMICAL PROVINCES, IN % OF DRY MATERIAL*

Region	Type soil	Infiltrated Province			Control Region		
		Mo	Cu	Mo:Cu	Mo	Cu	Mo:Cu
Ankavan	Mountain meadow	$3.4 \cdot 10^{-3}$ ($3.8 \cdot 10^{-4}$ - $6.4 \cdot 10^{-3}$)	$5.3 \cdot 10^{-4}$ ($2.5 \cdot 10^{-4}$ - $1.0 \cdot 10^{-3}$)	6.4:1	$7.3 \cdot 10^{-5}$ ($1.9 \cdot 10^{-5}$ - $1.3 \cdot 10^{-4}$)	$3.4 \cdot 10^{-4}$ ($1.5 \cdot 10^{-4}$ - $5.9 \cdot 10^{-4}$)	1:4.6
	Brown mountain forest	$1.3 \cdot 10^{-3}$ ($2.6 \cdot 10^{-4}$ - $4.0 \cdot 10^{-3}$)	$7.7 \cdot 10^{-4}$ ($3.3 \cdot 10^{-4}$ - $1.5 \cdot 10^{-3}$)	1.7:1	$3.2 \cdot 10^{-5}$ ($2.1 \cdot 10^{-5}$ - $5.3 \cdot 10^{-5}$)	$5.8 \cdot 10^{-4}$ ($4.1 \cdot 10^{-4}$ - $7.6 \cdot 10^{-4}$)	1:18.1
	Waterlogged	$2.3 \cdot 10^{-3}$ ($1.4 \cdot 10^{-3}$ - $3.6 \cdot 10^{-3}$)	$2.9 \cdot 10^{-4}$ ($1.3 \cdot 10^{-4}$ - $5.1 \cdot 10^{-4}$)	8.0:1	-- ($3.8 \cdot 10^{-5}$ - $1.1 \cdot 10^{-4}$)	-- ($1.7 \cdot 10^{-4}$ - $2.0 \cdot 10^{-4}$)	--
Mean for the province		$2.6 \cdot 10^{-3}$	$5.7 \cdot 10^{-4}$	4.6:1	$6.1 \cdot 10^{-5}$	$4.0 \cdot 10^{-4}$	1:6.6
Kadzharan	Chestnut	$2.9 \cdot 10^{-3}$ ($1.1 \cdot 10^{-3}$ - $5.1 \cdot 10^{-3}$)	$1.3 \cdot 10^{-2}$ ($4.1 \cdot 10^{-3}$ - $2.0 \cdot 10^{-2}$)	1:4.5	$1.2 \cdot 10^{-4}$ ($4.0 \cdot 10^{-5}$ - $3.1 \cdot 10^{-4}$)	$6.7 \cdot 10^{-4}$ ($1.7 \cdot 10^{-4}$ - $2.0 \cdot 10^{-3}$)	1.56
	Gray mountain forest	$3.0 \cdot 10^{-3}$ ($9.7 \cdot 10^{-4}$ - $5.5 \cdot 10^{-3}$)	$2.2 \cdot 10^{-2}$ ($4.3 \cdot 10^{-3}$ - $3.5 \cdot 10^{-2}$)	1:7.0	--	--	--
Mean for the province		$2.9 \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$	1:5.9	--	--	--

Table 1 continued

Dastakert	Chestnut	$(4.9 \cdot 10^{-3} - 2.4 \cdot 10^{-2})$	$(5.8 \cdot 10^{-2} - 8.8 \cdot 10^{-2})$	--	$(2.7 \cdot 10^{-4} - 4.9 \cdot 10^{-4})$	$(2.7 \cdot 10^{-3} - 3.0 \cdot 10^{-3})$	--
	Mountain meadow	$(1.7 \cdot 10^{-3} - 1.3 \cdot 10^{-2})$	$(5.0 \cdot 10^{-2} - 9.6 \cdot 10^{-2})$	--	$(2.2 \cdot 10^{-4} - 2.7 \cdot 10^{-4})$	$(4.2 \cdot 10^{-3} - 4.9 \cdot 10^{-3})$	--
Mean for the province		$8.6 \cdot 10^{-3}$	$7.2 \cdot 10^{-2}$	1:8.4	$3.1 \cdot 10^{-4}$	$3.7 \cdot 10^{-3}$	1:11.9

*Limits of variations are shown in parentheses.

Table 2 continued

Dastakert	Chestnut	$(8.9 \cdot 10^{-4} - 4.3 \cdot 10^{-3})$	$(7.0 \cdot 10^{-3} - 9.9 \cdot 10^{-3})$	--	$(6.4 \cdot 10^{-5} - 9.7 \cdot 10^{-5})$	$(3.6 \cdot 10^{-4} - 3.9 \cdot 10^{-4})$	--
	Mountain meadow	$(2.6 \cdot 10^{-4} - 1.9 \cdot 10^{-3})$	$(5.1 \cdot 10^{-2} - 8.6 \cdot 10^{-3})$	--	$(4.9 \cdot 10^{-5} - 5.2 \cdot 10^{-5})$	$(3.9 \cdot 10^{-4} - 5.5 \cdot 10^{-4})$	--
Mean for the province		$1.4 \cdot 10^{-3}$	$7.3 \cdot 10^{-3}$	1:5.2	$6.5 \cdot 10^{-5}$	$4.2 \cdot 10^{-4}$	1.65

*Limits of variations are shown in parentheses.

Attempts to establish some kind of behavior pattern in the distribution of molybdenum in the vertical profile of soils as a function of pH were unsuccessful. The acidified humus horizon often will contain more molybdenum than the more alkaline lower-lying horizons. The molybdenum distribution-soil profile curve follows the pH distribution curve in some sections only.

Copper storage is somewhat greater in the forest soils of the province than in the mountain meadow soils, with the result that there is a change in the ratios between Mo and Cu contents. This can be the result of some reduction in the mobility of the molybdenum, and of an increase in the mobility of the copper, in brown forest soils as compared to mountain meadow soils. It is possible that the principal factor here is the pH value.

The distribution of molybdenum and copper through the vertical profile of soils can be determined by the storage of these elements by plants, and by their content in the rock. On this score, there are two maxima for increased content of metals in the majority of the soil sections. The first of these maxima is confined to the A horizon, the second to the C horizon, but the second maximum for molybdenum is greater than the first in the molybdenum-infiltrated province. Contrariwise, the first maximum is greater than the second in the soils outside the province. The second maximum is greater than the first for copper in either case. Copper evidently is a less mobile element than molybdenum under the conditions given. The molybdenum content maximum for waterlogged soils shifts downward through the profile to a depth of 20-30 cm.

Accordingly, the soils in the Ankavan region that have formed over the molybdenum-infiltrated rocks contain a large quantity of this element. The molybdenum dispersion halo is small (10-50 m), given the conditions that exist in the province under study, and depends on the steepness of slopes, and on other relief features. The molybdenum content maximum usually shifts slightly down the slope as a result of soil shattering, and of soil particles and dissolved molybdenum compounds being transported with water flows.

Molybdenum in the province's natural waters. The waters in the province under study contain a greater quantity of molybdenum than do the waters in the control regions, and do so by an order of magnitude (Table 3), and are much more heavily infiltrated by this element than the mean for the molybdenum content in surface waters. The magnitude of the latter, according to data provided by Kuroda and Sandell [21], is a maximum of 1×10^{-7} percent.

The water in springs outside the province contain slight amounts of molybdenum. Spring water within the province used by the local population for drinking water contains up to 3.5×10^{-6} percent molybdenum. Mineral waters outwelling in the vicinity of the settlement of Ankavan too contain a substantial quantity of molybdenum (about 2×10^{-6} percent).

The content of copper in these waters is close to the mean content of copper in surface waters, and is equal to 2×10^{-6} percent [2]. The ratio of Mo to Cu in mine and other waters does not correspond to their ratio in rock, but always is several times greater, which too points to the great mobility of molybdenum, as compared with copper, in the oxidation zone.

Molybdenum in the plants in Ankavan province. Soils and waters are the habitats for the living organisms in which the characteristic features of their chemical composition form. Plants growing in the molybdenum-infiltrated soils in Ankavan province contain a great deal more molybdenum than those that grow in soils not infiltrated by molybdenum. The concentration of molybdenum in plants, calculated in terms of dry material, is n x 10^{-4} to n x 10^{-3} percent for the former, and n x 10^{-5} percent for the latter (Table 2).

The mean content of copper in plants in the molybdenum-infiltrated province, and in those outside the province, is very similar.

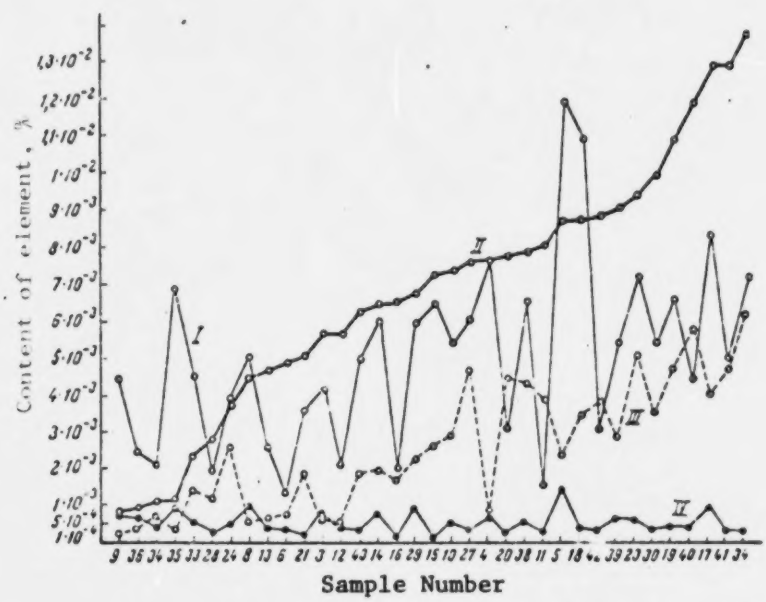

Figure 1. Content of copper and molybdenum in soils and plants in the Ankavan biogeochemical province. In soils: I - Cu; II - Mo. In plants: III - Mo; IV - Cu.

The compositions of the majority of the plants can be correlated to soil compositions in terms of molybdenum content, more or less (Figure 1). The greater the quantity of molybdenum in the soil, the greater the storage of the element in plants, but there is no direct and constant relationship between these phenomena. Soil pH, and the soil content in organic matter, copper, iron, manganese, phosphorus, sulfur, and others, influence the assimilation of molybdenum by plants. On the other hand, the concentration of molybdenum in plants depends on the physiological peculiarities of the organism that determine the latter's need for this element.

The influence of external factors associated with the environment can be illustrated quite well by the following example. Plants growing in a region's mountain meadow soils with the highest pH in soils in that region contain more molybdenum than do plants growing in brown mountain forest and waterlogged soils (Figure 2). The coefficient of concentration of molybdenum (the ratio of plant molybdenum content to soil molybdenum content) for plants growing in mountain meadow soils is 0.43, 0.24 for those plants growing in brown mountain forest soils, and 0.37 for those growing in waterlogged soils. Plants growing in acid waterlogged soils concentrate molybdenum better than do those growing in brown forest soils with less of an acid reaction. It is difficult to explain this phenomenon, because the study of the behavior of molybdenum in soils, and the reasons for its availability to plants, is far from complete. It seems obvious that factors can be present in the soil that will more actively influence the availability of molybdenum than the magnitude of the soil's pH. The presence in the soil of a great quantity of free hydrated oxides of iron, for example, will

Table 3

CONTENT OF MOLYBDENUM AND COPPER IN THE WATERS OF THE PROVINCES, %

Region	Water	Infiltrated Province		Control Region	
		Mo	Cu	Mo	Cu
Ankavan	River	$2 \cdot 10^{-6} - 8 \cdot 10^{-5}$	$- 1 \cdot 10^{-5}$	$2.0 \cdot 10^{-7} - 5.0 \cdot 10^{-7}$	$- 1.1 \cdot 10^{-6}$
	Spring	$1.4 \cdot 10^{-6} - 3.5 \cdot 10^{-6}$	$9.0 \cdot 10^{-7} - 3.0 \cdot 10^{-6}$	$3.3 \cdot 10^{-7} - 1.3 \cdot 10^{-6}$	$8.9 \cdot 10^{-7} - 3.6 \cdot 10^{-6}$
	Mine	$5.3 \cdot 10^{-5} - 4.0 \cdot 10^{-4}$	$9.3 \cdot 10^{-7} - 1.5 \cdot 10^{-5}$	--	--
	River	$1.7 \cdot 10^{-6} - 2.0 \cdot 10^{-6}$		$4.7 \cdot 10^{-7} - 1.8 \cdot 10^{-6}$	$- 6.7 \cdot 10^{-7}$
Kadzharan	Spring	$1.2 \cdot 10^{-6} - 3.1 \cdot 10^{-5}$	$- 7.0 \cdot 10^{-5}$	$- 1.1 \cdot 10^{-7}$	$- 2.3 \cdot 10^{-6}$
	Mine	$5.7 \cdot 10^{-6} - 8.9 \cdot 10^{-5}$	$1.4 \cdot 10^{-5} - 2.8 \cdot 10^{-5}$	--	--
Dastakert	River	$1.0 \cdot 10^{-6} - 1.3 \cdot 10^{-6}$	$4.1 \cdot 10^{-7} - 4.9 \cdot 10^{-7}$	$5.4 \cdot 10^{-7}$	
	Spring	$3.2 \cdot 10^{-6} - 4.2 \cdot 10^{-6}$	$5.6 \cdot 10^{-6} - 6.2 \cdot 10^{-6}$	$8.1 \cdot 10^{-7}$	$5.3 \cdot 10^{-7}$

make soil molybdenum poorly available for plants, even in slightly alkaline soils [17, 22]. It can be assumed, therefore, that the organic matter in soils that waterlogged soils are rich in form those compounds with molybdenum that are available to plants, or which readily release molybdenum, even when the conditions are those of an acid reaction.

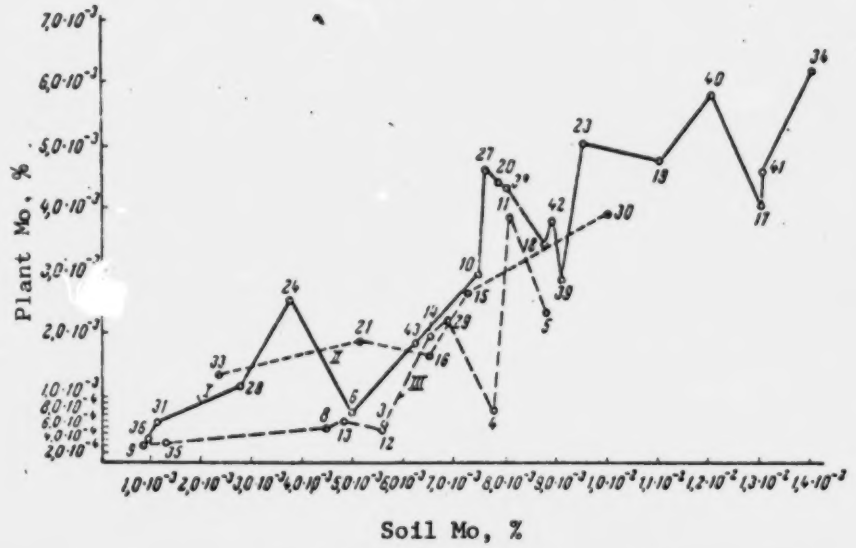

Figure 2. Content of molybdenum in plants in different types of soils (Ankavan province). Sample numbers on the curves are for I - mountain meadow soils, II - waterlogged soils; III - brown mountain forest soils.

The relationship between the degree of concentration of molybdenum in plants and type of soil in regions where the soil is not enriched with molybdenum is similar, but the coefficient of concentration of molybdenum in this case is lower than in a province in which the soil is infiltrated by molybdenum. This coefficient is 0.21 for plants growing in mountain meadow soils, and 0.15 and 0.25, respectively, for plants growing in brown mountain forest and waterlogged soils. The reactions of soils from

an enriched zone, and outside such a zone, are approximately the same, so the difference in the degree of concentration of molybdenum in plants can, evidently, be equated to the dissimilar ratios of molybdenum and copper in the soils. Molybdenum cannot be assimilated as well by plants where the copper content is relatively high. Several authors have pointed out the limiting influence molybdenum has on the entry of copper into a plant [23-25].

Copper concentrations are higher in plants in the region under study growing in brown mountain forest soils than in those growing in mountain meadow soils, and are least in plants collected from waterlogged soils (Figure 3). Copper, as distinguished from molybdenum, concentrates well in plants growing in the more acid soils. Soils with high pH values tend to retain copper more tenaciously, and thus the assimilation of copper by plants is poor [26, 27]. Plants growing in waterlogged soils show lower concentrations of copper than do those growing in the other soils, despite the acid reaction. This can be explained by the strong bond between copper and the organic matter which is in a much greater concentration here than in mountain meadow and mountain forest brown soils. The result is that copper will form compounds that are unavailable to plants. We know that copper will form very strong compounds with humus soils, the nature of which will depend on the properties of the organic matter. Antipov-Karatayev [29], studying the exchange sorption of bivalent copper in different soils, found that the more intensively the copper ions bond with heavily humus soils the stronger the compounds they form in those soils, as compared to the compounds in minerals.

The fact that the Mo:Cu ratio is higher in plants than it is in the soil also is indicative of the reduced availability of copper to the plants as compared to the availability of molybdenum, given the conditions in the region under study.

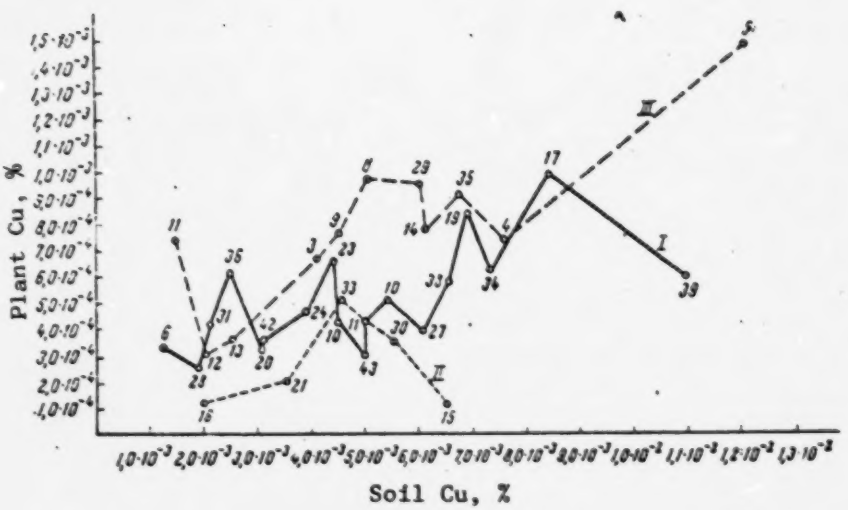

Figure 3. Content of copper in plants in different types of soils (Ankavan province). I - mountain meadow soils; II - waterlogged soils; III - brown mountain forest soils.

The influence of the factors associated with the physiology of plants is evident from the fact that not all plants growing in areas with a high molybdenum content store this element in large quantities. Vinogradova [30] shows that representatives of the legume family are molybdenum concentrators. Legume ash molybdenum content can be measured in the hundreds and thousandths of a percent under ordinary conditions when soil molybdenum content is comparatively low. The results of our analyses once again confirm the correctness of this conclusion. In addition to the legume family,

representatives of the figwort, mint, and aster families store a considerable quantity of this element, whereas gramen and woody plants store the least (Table 4).

The broad propagation, and the abundance and strong development of legumes, on the territory of a molybdenum province probably is associated with the elevated content of molybdenum in the environment, something not observed in control regions that are very similar in terms of natural conditions.

Variations in molybdenum content in plants of the same species are quite wide and are attributed to the content of this element in the soils, and to the availability of the element to the plants as a result of soil conditions (Figure 4).

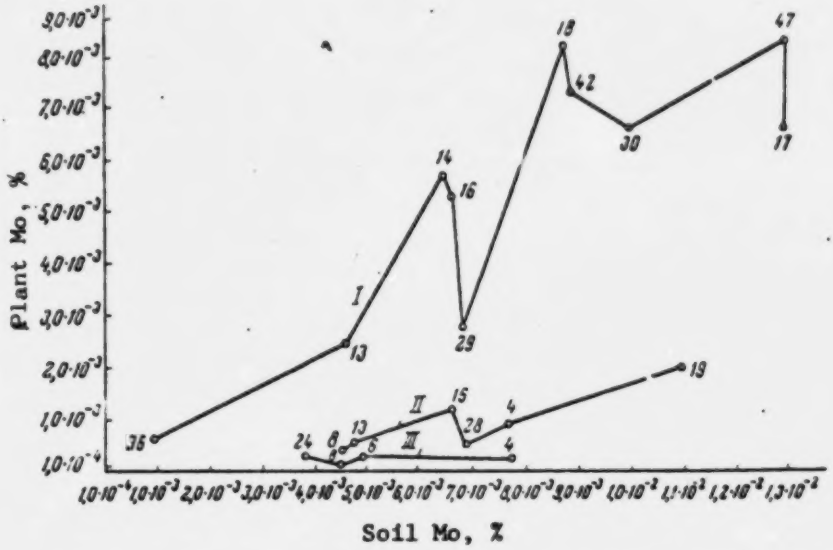

Figure 4. Content of molybdenum in plants of individual species. I - Trifolium medium L; II - Myosotis alpestris Schicht; III - Poa bulbosa L.

Table 4

MEAN CONTENT OF MOLYBDENUM AND COPPER IN PLANTS OF DIFFERENT FAMILIES IN THE ANKAVAN REGION, % OF DRY WEIGHT

Family		No. specimens	Molybdenum Province		No. specimens	Control Region	
			Mo	Cu		Mo	Cu
Ranunculaceae	- crowfoot	6	$1.9 \cdot 10^{-3}$	$4.8 \cdot 10^{-3}$	4	$2.7 \cdot 10^{-5}$	$4.4 \cdot 10^{-4}$
Rosaceae	- rose	9	$1.4 \cdot 10^{-3}$	$4.2 \cdot 10^{-4}$	4	$4.7 \cdot 10^{-5}$	$3.6 \cdot 10^{-4}$
Leguminosae	- legume	35	$4.6 \cdot 10^{-3}$	$8.0 \cdot 10^{-4}$	10	$2.6 \cdot 10^{-4}$	$6.3 \cdot 10^{-4}$
Umbelliferae	- umbrella-shaped	14	$2.0 \cdot 10^{-3}$	$8.4 \cdot 10^{-4}$	5	$5.2 \cdot 10^{-5}$	$4.9 \cdot 10^{-4}$
Fagaceae	- beech	5	$3.9 \cdot 10^{-4}$	$3.7 \cdot 10^{-4}$	3	$4.7 \cdot 10^{-5}$	$3.4 \cdot 10^{-4}$
Borraginaceae	- borage	10	$1.7 \cdot 10^{-3}$	$4.2 \cdot 10^{-4}$	6	$5.7 \cdot 10^{-5}$	$5.9 \cdot 10^{-4}$
Scrophulariaceae	- figwort	6	$3.8 \cdot 10^{-3}$	$4.8 \cdot 10^{-4}$	3	$9.1 \cdot 10^{-5}$	$5.3 \cdot 10^{-4}$
Labiatae	- mint	11	$2.7 \cdot 10^{-3}$	$9.2 \cdot 10^{-4}$	6	$7.9 \cdot 10^{-5}$	$5.8 \cdot 10^{-4}$
Papaveraceae	- poppy	3	$2.2 \cdot 10^{-3}$	$5.6 \cdot 10^{-4}$	2	$6.2 \cdot 10^{-5}$	$8.4 \cdot 10^{-4}$
Companulaceae	- bell-flower	8	$3.6 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	2	$3.3 \cdot 10^{-5}$	$5.7 \cdot 10^{-4}$
Compositae	- aster	19	$3.1 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	6	$8.7 \cdot 10^{-5}$	$5.4 \cdot 10^{-4}$
Caryophyllaceae	- pink	7	$1.3 \cdot 10^{-3}$	$5.1 \cdot 10^{-4}$	2	$3.7 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$
Polygonaeceae	- buckwheat	9	$1.6 \cdot 10^{-3}$	$3.2 \cdot 10^{-4}$	3	$2.3 \cdot 10^{-5}$	$2.9 \cdot 10^{-4}$
Gramineae	- grass	23	$2.4 \cdot 10^{-4}$	$4.7 \cdot 10^{-4}$	19	$1.2 \cdot 10^{-5}$	$2.1 \cdot 10^{-4}$

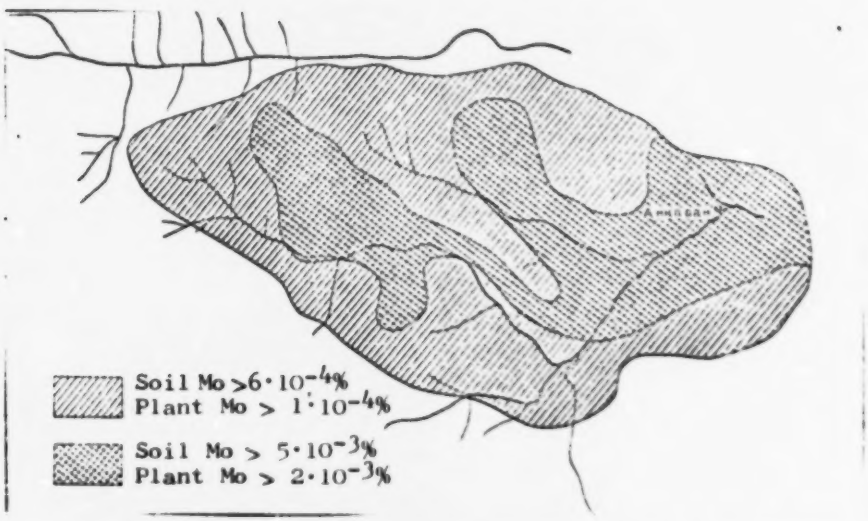

Figure 5. Choropleth map of a biogeochemical province with elevated content of molybdenum in the Ankavan region.

No diseases, or changes in the forms of plants, that could be related to the high content of molybdenum in their organism were detected in the regions in the province studied. This accords with the known data in the literature [31, 32] that indicate that plants are capable of transporting high concentrations of molybdenum (in the tenths of a percent by dry weight) without apparent changes, and further that they become diseased if there is a lack of this element in the soil.

Despite some heterogeneity in storage, all soils and plants in a molybdenum-infiltrated rock zone contain an elevated quantity of this element. This fact is what has made it possible to single out a zone with a high content of molybdenum in soils, waters, and plants, and to determine the limits of the propagation of the molybdenum biogeochemical province in the Ankavan region (Figure 5).

Content and Migration of Molybdenum and Copper in Soils, Waters, and Plants in the Kadzharan Biogeochemical Province

The molybdenum content in the rocks of the Kadzharan region varies from 1.0×10^{-3} to 7.0×10^{-3} percent [33]. This elevated content in the rocks is reflected in the increase seen in the overall level of the concentration of disseminated molybdenum in soils, natural waters, and plants. The study of the behavior and content of molybdenum and copper in the Kadzharan biogeochemical province, and in the control regions, was based on the collection and analysis of 91 soil samples, 9 water samples, and 153 plant specimens.

Molybdenum in the province's soils. The content of molybdenum in the soils of the Kadzharan biogeochemical province is a mean of 1.1×10^{-2} percent, and varies from 3.6×10^{-3} to 2.0×10^{-2} percent, or greater than the mean content in the soils of the chernozem zone by a factor of 20-100 (Table 1). Malyuga [34] found that the magnitudes for soils in this province were very similar (from 2.0×10^{-3} to 3.0×10^{-2} percent).

The soils in the Kadzharan region differ from those in the Ankavan province in that they have a higher content of copper (2×10^{-3} percent), and the quantity of copper is considerably greater than the molybdenum content (Mo:Cu = 1:10.9).

The quantities of molybden and copper found in the soils of control sections are close to the mean content of these elements in the soils.

The variations found in molybdenum content in individual soil samples are the result of the different contents of molybdenum in the basement

rock, just as was the case in Ankavan province. Gray mountain forest soils contain more molybdenum, on the average, than do the more alkaline chestnut soils, despite the somewhat greater acid reaction of the environment. This is the result, in all likelihood, of the fact that the gray mountain forest soils have developed in greatly changed monzonites containing the greatest quantity of molybdenum (about 7.0×10^{-3} percent), at the same time that the chestnut soils took form in changed, as well as in unchanged, monzonites and porphyrites containing but 1.0×10^{-3} to 2×10^{-3} percent molybdenum [33].

The distribution of molybdenum with respect to the genetic horizons of the soils in the infiltrated region has the same behavior patterns as those noted in Ankavan province; elevated content of the element in the upper humus layer, reduction in the underlying horizon, and a new, sharp increase in the horizon close to the rock. The content of molybdenum in soils in sections outside the limits of the province decreases with depth. The slight shift in the molybdenum content maximum dowward along the slope of the mountains, despite the considerable steepness of the slopes, can be explained [33] by the limited range of the migration of high molybdenum concentrations, ones that are concentrated and firmly anchored in the soil humus layer and in the clay minerals of the eluvium. It is obvious that this is why the molybdenum dispersion halo in soils and plants does not extend very far from the infiltrated rocks.

The examples cited make it obvious that the migration of chemical elements in a soil layer cannot be uniquely determined by some one factor,

but rather that there is a whole complex of conditions, such as content of the element in the rock, the degree of development of the rock oxidation zone, the magnitude of the soil pH, the content of organic matter, terrain relief, moisture conditions, and the like, that have an influence on this process.

The diversity of natural conditions therefore must be taken into considerations when studying the behavior of a chemical element in predetermined zones.

Molybdenum in the province's natural waters. Surface, ground, and mine waters in the Kadzharan biogeochemical province are much more heavily infiltrated by molybdenum that are those waters found outside the boundaries of the province, as will be seen from the data listed in Table 3.

The ratio of molybdenum to copper in the waters increases as compared to their ratio in soil and rock, indicative of the high degree of mobility of molybdenum, as compared to copper, under the conditions prevailing in the province under study.

Molybdenum in the province's plants. Table 2 lists the mean content of molybdenum and copper in plants growing in the different kinds of soils in the province, and in the control regions. Plants in the province are quite heavily infiltrated by molybdenum (2.9×10^{-3} percent) and copper (1.7×10^{-2} percent). The data provided by Malyuga [33] show the molybdenum content in the ash of plants from this region as varying from 2.0×10^{-3} to 4.0×10^{-2} percent.

The change that takes place in the molybdenum-copper ratio in plants (1:5.9), as compared to that in the soil (1:10.9), is indicative of the great mobility of molybdenum as compared to that of copper. However, the coefficient of concentration of molybdenum in plants in the Kadzharan region (0.26) is less than it is in the Ankavan province (0.46), despite the fact that the soils in the Kadzharan province have a greater alkaline reaction. This is the result of the influence of the great quantities of copper occurring in the soils of Kadzharan province, thus reducing the availability of molybdenum to plants.

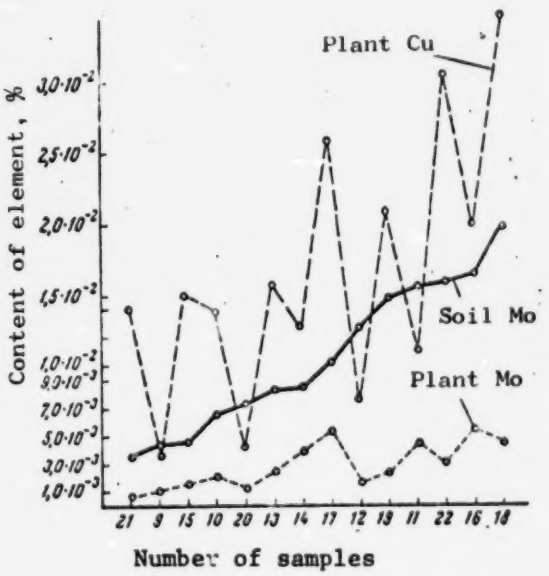

Figure 6. Content of molybdenum and copper in soils and plants in the Kadzharan biogeochemical province.

The content of molybdenum and copper in plants depends on the content of these elements in the soil (Figure 6). As was the case in Ankavan province, pH and copper content in the soil influence the quantity of

molybdenum in plants. But it should be pointed out that there are factors other than those cited in the foregoing that determine the content of molybdenum in plants. There are still a great many unanswered questions that are concerned with the availability to plants of this element. Almost all of the plants in the province are richer in molybdenum by a while order of magnitude than the mean content of molybdenum in plants collected outside the limits of the province. The greatest quantity of molybdenum is concentrated in representatives of the legume, mint, and figwort families, and the least in the gramen and woody plants, just as was the case in the Ankavan province (Table 5).

Malyuga et al. [34], conducting geobotanical research in the Kadzharan region, turned their attention to the preferred spread of hillside milk vetch (Astragalus declinatus) over the zones of copper-molybdenum deposits and advanced the view that what is taking place here is the biogeochemical adaptation of a particular specie of plant to a zone of mineralization. Chemical analysis of the milk vetches showed high molybdenum and copper contents. Nevertheless, there were other plants growing on the molybdenum-infiltrated rocks, such as figwort, St. Johnswort, thyme, and many others, that had stored molybdenum to the same degree. So the extent of the hillside milk vetch cannot be explained simply by the high content of molybdenum in the soils. Instead what must be taken into consideration is the influence of a whole complex of soil, climatic, and geochemical conditions. These same authors found a changed form of poppy (Papaver commutatum F. and M.), one with an unusually heavy development of black

Table 5

MEAN CONTENT OF MOLYBDENUM AND COPPER IN PLANTS OF CERTAIN FAMILIES IN THE KADZHARAN REGION, % OF DRY WEIGHT.

Family		Molybdenum province			Control Region		
		No. specimens	Mo	Cu	No. specimens	Mo	Cu
Rosaceae	- rose	3	$1.3 \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$	5	$7.7 \cdot 10^{-5}$	$5.4 \cdot 10^{-4}$
Leguminosae	- legume	15	$5.9 \cdot 10^{-3}$	$2.8 \cdot 10^{-2}$	9	$3.0 \cdot 10^{-4}$	$2.5 \cdot 10^{-3}$
Scrophulariaceae	- figwort	6	$4.2 \cdot 10^{-3}$	$2.1 \cdot 10^{-2}$	2	$1.2 \cdot 10^{-4}$	$7.2 \cdot 10^{-4}$
Labiatae	- mint	10	$5.0 \cdot 10^{-3}$	$2.4 \cdot 10^{-2}$	6	$1.1 \cdot 10^{-4}$	$6.4 \cdot 10^{-4}$
Papaveraceae	- poppy	3	$2.2 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	2	$6.7 \cdot 10^{-5}$	$3.9 \cdot 10^{-4}$
Compositae	- aster	9	$2.6 \cdot 10^{-3}$	$1.9 \cdot 10^{-2}$	4	$6.5 \cdot 10^{-5}$	$4.9 \cdot 10^{-4}$
Caryophyllaceae	- pink	4	$1.0 \cdot 10^{-3}$	$8.8 \cdot 10^{-3}$	4	$4.6 \cdot 10^{-5}$	$5.6 \cdot 10^{-4}$
Gramineae	- grass	14	$3.0 \cdot 10^{-4}$	$2.2 \cdot 10^{-2}$	12	$2.9 \cdot 10^{-5}$	$5.9 \cdot 10^{-4}$

coloration of the petals, in the Kadzharan province area. The authors hypothesize that this form of poppy adapted to the outwelling of ground waters rich in copper and molybdenum because it was found in a sector where the soils are saturated with ground waters enriched with these elements. A metamorphosis in the shade of colors under the influence of chemical factors is a rather frequent phenomenon. However, the comparatively small content of copper (0.021 percent) and molybdenum (0.006 percent) in the ash of the changed poppy is not sufficient reason for the authors to assert that the phenomenon they observed was entirely attributable to the presence of these elements. There are other, local, geochemical factors, such as the relative moisture content of the soils as a result of the outwelling of ground waters, and the reduction in the pH of these waters, that play a simultaneous role.

In addition to what has been said, there were no morphological changes, or diseases, associated with the high molybdenum content in the plants from the province studied, despite the fact that there was a considerable quantity of this element concentrated in the tissues of the plants.

The result of the research conducted in the Kadzharan region was the delineation of a province in which the soils, waters, and plants are enriched with molybdenum and copper (Figure 7). We too, in our mapping of the province, used data furnished by Malyuga [33] and his coworkers [34], all of whom studied the content of molybdenum and copper in the soils, waters, and plants in this region in connection with a study of the applicability of the biogeochemical method for prospecting for ore deposits.

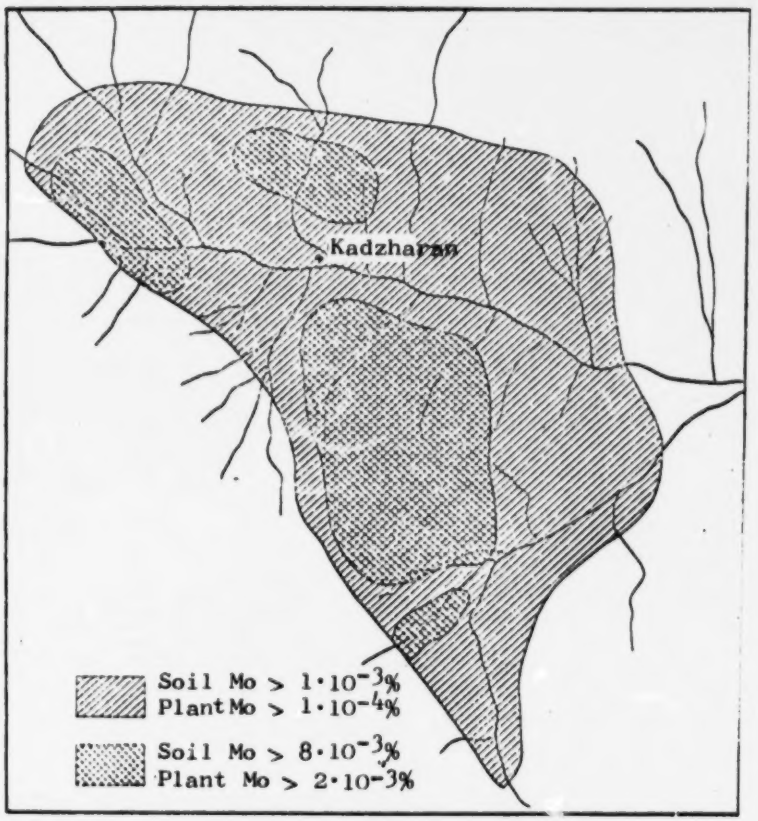

Figure 7. Choropleth map of a biogeochemical province with elevated content of molybdenum in the Kadzharan region.

Availability of Molybdenum and Copper to Plants in the Soils of the Province Studied

The content of molybdenum and copper in the plants in the regions studied usually concord with their content in the soil, but a direct and constant relationship cannot always be maintained because the total content of the element in the soil does not mandatorily correspond to the quantity of element available to the plants. Availability depends on the form of the compound of the element found in the soil and is determined by the

soil redox processes and reactions, by the presence of associated ions, by the quantity of organic materials, and so on. There is no doubt that water-soluble molybdenum is available to plants, but is present in the majority of soils in insignificant quantities [35]. Other forms of molybdenum (sorbed by soil colloids bonded to an organic material) also can be available under definite conditions. The forms in which molybdenum is found in soils have not been the subject of adequate study, and this is true of the majority of the other trace elements as well.

There is no generally accepted procedure for determining the molybdenum available to plants. The most widely used of the existing procedures is Grigg's oxalate method [14, 19, 20], one that has many advantages over methods for determining the availability of elements by extracting them with strong mineral acids. The use of the latter shed little light on the problem of the availability of the element because the conditions that are created in the presence of such acids are a long way from the conditions that exist in the soil.

Substances (organic acids) are produced in the process of the plant's life activity that cause the plant to put out roots and help extract a number of elements from the soil, converting their compounds from insoluble to soluble ones available to the plants. It is, therefore, more desirable to use a mixture of several organic acids to extract available elements from the soil, rather than a single organic acid, as is the case when Grigg's method is used.

The method proposed by V. V. Koval'skiy for extracting elements from the soil uses a moderate concentration of a mixture of organic acids, thus approaching, at least to some degree (and far from completely, of course), the natural conditions under which plants consume chemical elements in the soil, conditions that prevail at the site where soil particles and the plant's root system are in contact.

We undertook to determine the quantity of mobile molybdenum and copper by extracting these elements from the soil with a series of solvents and then checking to see whether or not the quantity of the element present in the extract corresponded to its quantity in the plants.

Determination of available molybdenum and copper was made using soil samples from seven soil profiles in the Nakavan region (three of which were from an infiltrated region, and four from a control), and two profiles from the Kadzharan biogeochemical province. Determinations were made of the quantity of molybdenum and copper passing over in an aqueous extract (pH 5.2), in a weakly alkaline solution (pH 7.5), in an extract of a mixture of organic acids with a concentration of 0.2 M (citric, oxalic, acetic, and tartaric), in 0.2 M solutions of each of the acids comprising the mixture. Table 6 lists the data obtained.

Some of the behavior patterns in the distribution of molybdenum between the soil and the plant are retained, just as they are in the distribution of molybdenum between the soil and a number of the solvents. The quantity of available elements usually increases with increase in its total content in the soils we studied, for example. Molybdenum passes

Table 6

EXTRACTION OF MOLYBDENUM AND COPPER FROM SOIL WITH VARIOUS SOLVENTS, % OF TOTAL CONTENT

Extract	Mo	Cu	Extract	Mo	Cu
Aqueous (pH 5.2)	1 - 4	0.5 - 2	Citric acid	5 - 12	4 - 6
Aqueous (pH 7.5)	2 - 7	0.5 - 3	Oxalic acid	50 - 70	5 - 10
Mixture of organic acids	16 - 40	3 - 8	Acetic acid	1 - 2	1 - 1.5
Hydrochloric acid	2 - 8	3 - 6	Tartaric acid	10 - 17	3 - 5

into the extract in greater quantity than does copper. Molybdenum can be better extracted from soils with a greater alkaline reaction than from soils with lower pH values. Molybdenum extraction from soils containing relatively more copper is poorer than from soils with relatively lower copper contents. These behavior patterns show up with particular clarity when the elements are extracted with water, and with a mixture of organic acids.

The maximum quantity of molybdenum passes into the oxalic acid extract, with the quantity of the element in the extract exceeding its content in plants. The high degree of solubility in this particular case can be explained by the formation of a strong molybdenum oxalate complex, one with the composition $MoO_3 \cdot C_2H_5O_4$, for example [36]. The molybdenum adsorbed by soil colloids and clays also can be bonded with oxalate ions.

The best correlation between the content of molybdenum in the extract is found in plants when soils are extracted with a mixture of organic acids. This correlation will not be found for copper, and here what is required, apparently, is a stronger acting solvent. The use of a mixture of organic

acids can be recommended for determining the molybdenum in the soil that is available to plants.

Reaction of Animals to a High Molybdenum Content in the Environment

The level of the content of a chemical element in the environment, as well as a definite reaction of living organisms populating the province to the prevailing level of the particular chemical element, indicate the existence of a biogeochemical province. These two basic criteria (the anomaly of the chemical composition of the environment, and reaction of living organisms) determine the presence of a biogeochemical province.

The high content of molybdenum in the soils of the provinces studied causes no marked changes in the life activity of the plants, if one ignores the quite large quantities of this element they have concentrated. Because the content of molybdenum in plants reaches magnitudes that ought to be, at least according to the data in the literature on the subject, toxic to animals, one ought to anticipate the appearance in the animals in these regions of symptoms of molybdenosis.

Plants containing 6.0×10^{-4} to 1.4×10^{-3} percent (dry material) molybdenum can cause symptoms of molybdenosis [37]. Attention was given to the similarity between the symptoms of animals suffering from molybdenosis and the symptoms of copper deficiency. This led to the successful use of copper to treat animals suffering from molybdenosis [7, 38]. The addition of copper to the ration for sick animals resulted in intensive elimination of molybdenum from the organism, and to recovery of the animals. No one has yet explained the mechanism involved in the physiological

reaction between molybdenum and copper, nor the toxic effect of molybdenum, but the physiological function performed by molybdenum in animals has been established. In this connection, we studied the daily rations and the molybdenum-copper balance in animals in the molybdenum-infiltrated regions, and in the control regions, and we also determined the activity of the xanthine oxidase,[1] the content of molybdenum and copper in blood and tissues, and the content of uric acid in the blood and in the urine.[2]

Results of Clinical Examination of Animals

Clinical examination of animals in the regions of the Kadzharan and Dastakert biogeochemical provinces, and archive data held by the veterinary services, showed that no symptoms of disease associated with the toxic effect of large quantities of molybdenum had been observed in these regions. This can be explained by the fact that the pasture plants in these provinces contain large quantities of copper, that this content is several times that of the molybdenum content, and thus is capable of overcoming the toxic effect of the molybdenum.

It has been established that in the Ankavan province, where the molybdenum content is higher than the copper, when cattle are put out to pasture (in the spring) lands located on the territory of a molybdenum province the animals develop serious gastroenteritic disorders, and suffer a deterioration in the quality of their wool. These phenomena pass during

1. Determination of the activity of the xanthine oxidase was made under anaerobic conditions, using methylene blue as the hydrogen acceptor [39,40].
2. Uric acid was determined by phosphotungstic reagent followed by oxidation of the phosphotungstic blue with potassium ferricyanide [41-43].

the summer stay of the animals on pasture lands with a normal molybdenum content, but the above-indicated disorders will reoccur within 2 to 3 days after the cattle are once again driven to the "molybdenum" pasture lands. It is entirely possible that these disorders are the onset of symptoms of molybdenum poisoning. Proof of this can be obtained from the fact that the illness appears only when the animals are put out to graze on pasture lands infiltrated with molybdenum, and disappears when the animals are driven to pasture lands with a normal content of this element. Moreover, the symptoms of the disease appear in the animals between the second and fourth days after the cattle have begun to graze on the molybdenum pasture lands, and this is characteristic of molybdenosis. According to Cunningham [7], molybdenosis occurs quickly, on the first to the fifth days. Symptoms of molybdenum toxicosis that we observed in the Ankavan molybdenum province appeared for the most part among large-horned cattle, and in particular among the younger animals. Arrington and Davis [44], Britton and Goss [3], as well as others, tell us that the toxic effect of molybdenum appears to a different degree in different species of animals. Molybdenosis is much rarer among sheep than among large-horned cattle, with the younger animals particular susceptible to the disease. Pigs and horses do not suffer at all from molybdenosis. Finally, elimination of other possible causes (infection, poisonous grasses, and the like), and the clinical picture of the disease, similar to that of symptoms of molybdenosis, described in the literature, prove that sickness among the cattle in the region of the Ankavan biogeochemical province is related to the toxic effect of molybdenum.

Results of Biochemical Research

The activity of the xanthine oxidase in the tissues of animals that had grazed on pasture lands infiltrated by molybdenum proved to be elevated as compared to that in the control in all organs studied.

The increase in the activity of the xanthine oxidase in tissues correlates with the increase in the concentration of molybdenum, and the reduction in the content of copper, in these tissues. These changes are not reflected alike in animals from different molybdenum provinces. As one might expect, these changes were much sharper in Ankavan province, with its relatively higher content of molybdenum and lower content of copper, than in Kadzharan province, where the copper content is greater than the molybdenum. The activity of the xanthine oxidase among animals from the Ankavan province, for example, is increased by 106 percent in the liver, by 65 percent in the kidneys, by 170 percent in the mucous membrane of the small intestine, and by 206 percent in the milk. The activity of this enzyme is increased in these tissues by 34, 17, 37 and 49 percent, respectively, among the animals from the Kadzharan province.

The most extensive change in the activity of the xanthine oxidase was found in the milk of cows eating fodder from molybdenum-infiltrated pastures (Figure 8). The concentration of molybdenum in the milk of these animals was elevated by a factor of 4.7, on the average. The content of copper in the milk of these animals, as distinguished from the other tissues, was not decreased, but rather was increased by a factor of almost 2.

It is possible that this is the result of increased excretion of copper from the animal's body as the quantity of molybdenum in the food increased.

The increase in the activity of the xanthine oxidase is the result of its increased synthesis with increase in the concentration of molybdenum in tissues, because molybdenum is a mandatory component part of this enzyme. Increase in the activity of the xanthine oxidase under experimental conditions upon the addition of molybdenum to the rations fed to rats was demonstrated by the authors, who discovered molybdenum in the composition of the xanthine oxidase. There have been no such observations made under natural conditions. It was not until 1957-1958 that papers appeared [45, 46] confirming the fact that the activity of the xanthine oxidase in cow's milk is proportional to the molybdenum content in the milk, and that this latter in turn is determined by the quantity of molybdenum in the fodder.

Our experiments with the supplementary feeding of animals with molybdenum and copper are the basis for the assertion that the changes in the purine metabolism in animals is the result of the action of the large quantity of molybdenum supplied to the animal with the fodder.

The activity of the xanthine oxidase in the tissues of rams upon supplementary feeding with molybdenum (50 mg/d) increased as compared to the control by 153 percent in the liver, 77 percent in the kidneys, and by 298 percent in the mucous membrane of the small intestine. The increase in the activity of the enzyme resulted in doubling the molybdenum output, but introduction in the form of a molybdate salt resulted in a smaller increase in the activity than that found when the molybdenum was introduced with the fodder. There is the possibility that molybdenum obtained

by the animal in the form of a salt is not assimilated as well by the animal as is molybdenum obtained in the form of the compounds in which it is present in food plants. Subsequent addition of copper to the rations fed the animals reduced the activity of the xanthin oxidase, and the content of molybdenum in the tissues, almost to the norm.

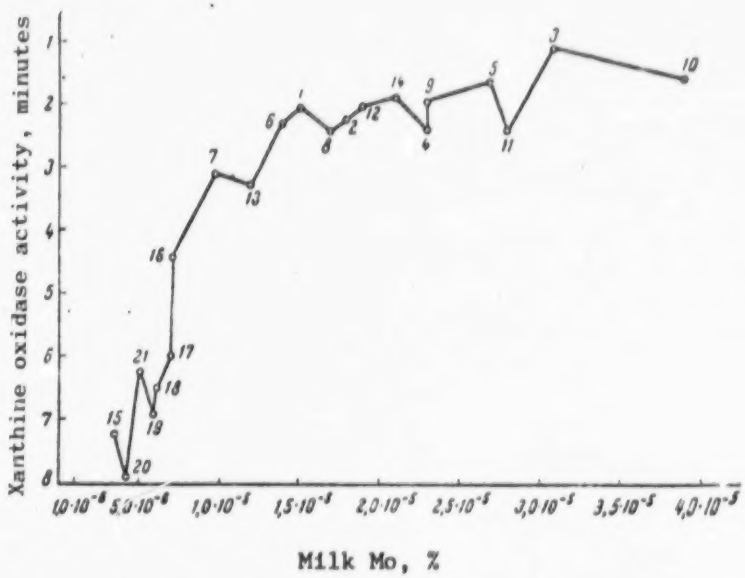

Figure 8. Activity of the xanthine oxidase, and content of molybdenum in cow's milk.

Despite the substantial increase in the activity of the xanthine oxidase in the tissues of the animals that had received an increased quantity of molybdenum, there was virtually no change in the blood uric acid concentration as compared to the control (Table 7). This does not mean, however, that the synthesis of uric acid in these animals took place to the same degree as in the control animals. The fact that uric

Table 7

MEAN CONTENT OF BLOOD URIC ACID AND ITS EXCRETION WITH THE URINE IN ANIMALS

Region	Animals	Molybdenum-infiltrated province			Control region		
		No. specimens	Blood uric acid, mg %	Urine uric acid, mg/d	No. specimens	Blood uric acid, mg %	Urine uric acid, mg/d
Ankavan	Calves	3	1.7	1.72	3	1.5	1.07
	Rams	5	1.1	0.71	4	0.9	0.26
Kadzharan	Rams	6	--	0.66	5	--	0.44
Dastakert	Rams	3	--	0.51	3	--	0.38

acid is not stored in the blood can be explained by possible intensification of the activity of the uricase upon increased formation of uric acid in the body and rapid oxidation of the latter into allantoin on the one hand, and by the increased elimination of uric acid from the body on the other.

Conduct of an equilibrium experiment established the fact that when animals were fed fodder from molybdenum-infiltrated pastures the storage of molybdenum increased by a factor of 7.1 in rams, and by a factor of 6 in calves as compared to normal conditions. The quantity of copper held in the body dropped quite sharply in the case of the calves (by a factor of 2.5), and there was a marked increase in its excretion with the urine. Our data concord with the observations of other authors who have studied the storage of copper in the body as a function of molybdenum content. The livers of animals that died of molybdenosis, for example, contained as much as 10 mg/kg dry material molybdenum when the norm is 0.2 mg/kg, and the copper content was reduced by a factor of 5-10 [37].

Change in the Purine Metabolism in Man Under Conditions Prevailing in a Molybdenum Biogeochemical Province

The animal research made it possible to pose the question of the influence an elevated concentration of molybdenum in the environment would have on purine metabolism in man, something that is of particular interest because of the lack of the enzyme uricase in the human body, according to accepted theory. Consequently, when there is an increase in the quantity of molybdenum, and an increase in the activity of the xanthine oxidase, in the human body, uric acid should be stored and should give

rise to symptoms of podagra [47]. The Ankavan molybdenum province was chosen for examinations because when there is an excess of molybdenum, and a relatively low copper content, one ought to expect much greater changes to take place in the purine metabolism. The following tasks were posed:

(1) medical examination of the inhabitants of a molybdenum biogeochemical province, in order to expose podagra type diseases;

(2) determine the quantities of molybdenum and copper entering the human body with food, given the conditions prevailing in the Ankavan molybdenum-infiltrated biogeochemical province, and the conditions prevailing in a control area with a normal molybdenum content;

(3) study the infiltration of the human body by molybdenum and copper by making a determination of the content of these elements in blood and urine when there is an elevated molybdenum content in food;

(4) investigate the content of uric acid in blood, and its excretion with urine;

(5) determine the activity of the blood xanthine oxidase;

(6) ascertain the nature of the correlation between the content of molybdenum in the food ration and in the blood, excretion of uric acid from the body, and the activity of the blood xanthine oxidase.

Four hundred persons from two settlements within the Ankavan province were examined. Dr. D. M. Shmavonyan, from the Institute of Health Resort Science of the Armenian Academy of Sciences, performed the clinical examinations of the inhabitants. It was established that clinical symptoms characterizing podagra were present in one of the settlements in 56

persons, or in 31 percent of the adult population examined, and in 14 persons, or in 18 percent of the adult population, in the other. These figures are extremely high, because according to the statistics no more than 1 to 4 percent of the people are afflicted with podagra.

A disease of the podagra type, as observed in a molybdenum biogeochemical province, is in the form of pains in the joints, particularly in the knee joints and in the metatarsophalangeal joints of the feet, and in the phalangeal joints of the hands. There are cases of a well-defined deformation of the joints, as well as of tumescence, an increase in temperature, and a reddening in the area of the joints. Acute seizures with increase in temperature are rare.

Fifty-two persons among the local inhabitants were given a thorough examination, as were five persons who did not live in this area (and who were used as the controls). Findings included content of molybdenum, copper, uric acid, and activity of the blood xanthine oxidase, as well as the daily excretion of molybdenum, copper, and uric acid with the urine.

The inhabitants of Ankavan eat what are primarily products of local origin and use large quantities of vegetable products in their diet (potatoes, lobi, bokhi, avelyuk, and others). The principal products eaten by the people living in the settlements indicated were studied for molybdenum and copper content, and these same studies were conducted for purposes of comparison in the control areas located outside the molybdenum province. Table 8 lists the results of the analyses.

Table 8

CONTENT OF MOLYBDENUM AND COPPER IN MAN'S FOOD PRODUCTS AND DRINKING WATER, %

(in the case of the vegetable products the calculations were made for the dry material, and in the case of the animal products for the raw product)*

Products	Molybdenum-infiltrated region		Region with normal molybdenum content	
	Mo	Cu	Mo	Cu
	Vegetable Products			
Potato	$1.1 \cdot 10^{-3}$	$3.2 \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$	$7.0 \cdot 10^{-4}$
Cabbage	$5.2 \cdot 10^{-4}$	$5.9 \cdot 10^{-4}$	$0.4 \cdot 10^{-5}$	$2.2 \cdot 10^{-3}$
Lettuce (kotim)	$7.3 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$4.8 \cdot 10^{-3}$
Tomatoes	$8.5 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	$2.7 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$
Eggplant	$1.3 \cdot 10^{-3}$	$8.7 \cdot 10^{-4}$	$9.7 \cdot 10^{-5}$	$9.3 \cdot 10^{-4}$
Lobi (Caucasian bean)	$8.2 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$5.1 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$
Bokhi	$2.1 \cdot 10^{-3}$	$4.4 \cdot 10^{-4}$	$9.0 \cdot 10^{-5}$	$5.1 \cdot 10^{-4}$
Avelyuk	$3.0 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$2.9 \cdot 10^{-5}$	$3.3 \cdot 10^{-4}$
Mint	$5.7 \cdot 10^{-3}$	$4.8 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	$7.7 \cdot 10^{-4}$
Chavek	$1.8 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$
Basil (rean)	$5.9 \cdot 10^{-4}$	$9.7 \cdot 10^{-4}$	$4.6 \cdot 10^{-5}$	$9.0 \cdot 10^{-4}$
Sabekh (sedge)	$9.3 \cdot 10^{-4}$	$1.0 \cdot 10^{-3}$	$7.3 \cdot 10^{-5}$	$1.5 \cdot 10^{-3}$
Tarkhun (tarragon)	$8.3 \cdot 10^{-4}$	$6.1 \cdot 10^{-4}$	$2.3 \cdot 10^{-5}$	$3.0 \cdot 10^{-4}$
Savzi (leek)	$1.0 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$	$9.7 \cdot 10^{-5}$	$1.2 \cdot 10^{-3}$
Bread, white, from imported flour	$5.1 \cdot 10^{-5}$	$2.1 \cdot 10^{-4}$	$3.9 \cdot 10^{-5}$	$2.8 \cdot 10^{-4}$
Bread, black	$2.8 \cdot 10^{-5}$	$7.4 \cdot 10^{-5}$	$4.1 \cdot 10^{-5}$	$5.9 \cdot 10^{-4}$
	Animal Products and Water			
Milk, cow's	$2.8 \cdot 10^{-5}$	$1.9 \cdot 10^{-5}$	$4.7 \cdot 10^{-6}$	$2.9 \cdot 10^{-5}$
Liver, beef	$3.4 \cdot 10^{-5}$	$2.1 \cdot 10^{-4}$	$9.8 \cdot 10^{-6}$	$1.1 \cdot 10^{-3}$
Liver, sheep	$2.4 \cdot 10^{-5}$	$1.7 \cdot 10^{-5}$	$8.6 \cdot 10^{-6}$	$7.4 \cdot 10^{-4}$
Meat, beef	$5.9 \cdot 10^{-6}$	$4.0 \cdot 10^{-5}$	$1.2 \cdot 10^{-6}$	$8.2 \cdot 10^{-5}$
Meat, sheep	$3.4 \cdot 10^{-6}$	$5.1 \cdot 10^{-5}$	$1.0 \cdot 10^{-6}$	$6.8 \cdot 10^{-5}$
Eggs	$8.1 \cdot 10^{-7}$	$4.9 \cdot 10^{-5}$	$3.4 \cdot 10^{-7}$	$9.1 \cdot 10^{-5}$
Water, drinking	$1.0 \cdot 10^{-6}$	$2.7 \cdot 10^{-5}$	$4.7 \cdot 10^{-7}$	$1.1 \cdot 10^{-5}$

*Translator's Note. Local product names have been transliterated. Equivalents, if any, are unknown.

The food products used by the inhabitants of the molybdenum province contain from 2 to 10 times as much molybdenum as do the products from the control regions. According to the information provided by the local inhabitants, products of local origin make up at least 50 percent of the total ration for a grown man. Based on analyses and questions put to the inhabitants, we calculated that the average adult in the zone of the Ankavan molybdenum province each day received in his food 10-15 mg of molybdenum and 5-10 mg of copper, whereas the norm outside the molybdenum province for the adult was 1-2 mg of molybdenum, and 10-15 mg of copper with his food.

The high content of molybdenum, and the relatively small quantity of copper, in the daily food ration have a definite influence on the concentration of molybdenum in the body, and this is reflected by the content in the blood and the excretion of molybdenum and copper with the urine. We observed elevated blood molybdenum, and some reduction in the copper concentration, as compared to the control in virtually all the inhabitants of the Ankavan biogeochemical province. The daily urine excretion usually contained an increased quantity of molybdenum and copper as compared to their content in the urine excreted by those in the control region.

The data thus obtained confirm the known fact that copper and molybdenum are antagonists within the animal organism. An increase in the food molybdenum content, and hence in tissue molybdenum content, results in a more intensive excretion of copper from the organism, and, further,

points to the possible storage of molybdenum in the human body, given conditions of an elevated content of molybdenum in the environment.

This provides the basis for the assumption that excess molybdenum can, in part, be needed for the synthesis of additional quantities of the enzyme xanthine oxidase. The increase in the blood xanthine oxidase can be judged from the results of the enzyme activity determination. The method we adapted to the determination of the activity of the xanthine oxidase under field conditions is based on the reaction of decolorization of methylene blue, so whole blood cannot be used to measure this activity. We therefore proceeded to measure the enzyme's activity in blood serum, using as our basis the xanthine oxidase site pointed out in the literature on the subject. The determination was made 30 minutes after withdrawal of blood from a vein (during which time the blood was kept at +5°).

The xanthine oxidase activity measurements involved 19 persons from the molybdenum province, and five from the control region (Table 9). Increase in enzyme activity ran parallel with the rise in blood molybdenum concentration, and provides grounds for the assumption that an increase in the quantity of molybdenum in the body (within the limits of the concentrations studied) will result in an increase in xanthine oxidase synthesis. There is a simultaneous drop in the Cu:Mo ratio. Figure 9 and 10 are the curves for this ratio. The variations shown by the curves can be explained by the individual peculiarities in metabolism in different people.

Table 9

ACTIVITY OF THE XANTHINE OXIDASE IN HUMAN BLOOD SERUM

Region	Objects of the study	Series no.	No. cases	Activity (in minutes) and reliability of difference					
				M	$\pm_\sigma$	$\pm_m$	t_{1-2}	t_{2-4}	t_{3-4}
Molybdenum province	Sick	1	8	4.77	0.53	0.189			
	Healthy	2	11	7.89	0.97	0.293	8.9	3.3	4.5
	Mean	3	19	6.59	2.17	0.491			
Control region	Controls	4	5	10.19	1.41	0.641			

Note. Here, and in the table that follows, M is the arithmetic mean; σ is the mean square deviation; m is the mean error; t is the reliability criterion.

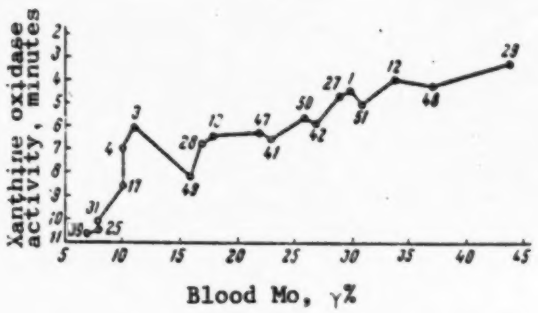

Figure 9. Xanthine oxidase activity and human blood molybdenum content.

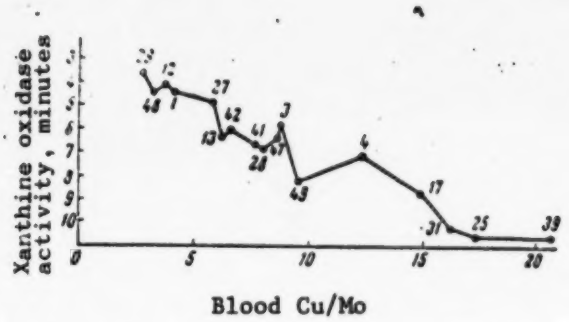

Figure 10. Xanthine oxidase activity as a function of the blood Cu:Mo ratio.

The correlation thus established between elevated blood molybdenum content, reflecting as it does the overall storage of molybdenum in the body, and the xanthine oxidase activity, is extremely important to an understanding of the purine metabolism processes that take place in a molybdenum province.

Increased xanthine oxidase activity should help in the formation of uric acid in the body, and this was found to be so experimentally. The uric acid concentration (Table 10) increases along with increase in the xanthine oxidase activity, reaching a figure of 10-11 mg% as opposed to a norm of 3-5.5 mg% [48-50]. The changes that occur in the purine metabolism in definite body tissues are reflected in the blood picture. It is only natural that the relationship between the uric acid and the molybdenum in the blood be quite pronounced under these conditions (Figure 11).

Table 10

CONTENT OF URIC ACID IN HUMAN BLOOD AND URINE

Region	Objects of the study	Series no.	Blood							Urine						
			No. cases	Uric acid content, M, mg %	$\pm\sigma$	$\pm m$	t_{1-2}	t_{2-4}	t_{3-4}	No. cases	Uric acid quantity, M, mg/day	$\pm\sigma$	$\pm m$	t_{1-2}	t_{2-4}	t_{3-4}
Molybdenum province	Sick	1	17	8.1	1.77	0.43	5.1	2.6	4.4	17	823.8	284.8	67.2	2.2	3.9	4.9
	Healthy	2	35	5.3	2.09	0.35				34	648.7	233.5	39.6			
	Mean	3	52	6.2	2.3	0.32				51	707.0	246.8	42.5			
Control region	Controls	4	5	3.8	1.01	0.46				5	432.1	88.6	40.3			

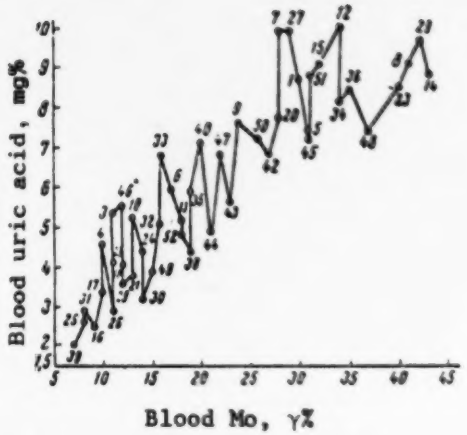

Figure 11. Uric acid content as a function of blood molybdenum.

Symptoms of podagra coincided with elevated blood uric acid content in the overwhelming majority of cases. The mean relationship between blood uric acid content and the time those studied had lived in the Ankavan molybdenum province was established as follows: up to one year 3.75 mg%; from 1 to 5 years 6.4 mg%; and from 5 years on up 6.8 mg%. It seems quite evident that changes take place quite rapidly, perhaps even during the first year of residence in this particular region.

The excretion of uric acid with urine in the persons studied was for the most part within limits of the norm, and as a rule increased somewhat with increase in the blood uric acid concentration (Table 10).

Molybdenum toxicosis in animals can be treated by adding copper to the fodder, with a resultant increase in the excretion of molybdenum from the organism. It is entirely probable that small additions of copper to the human diet could increase the excretion of molybdenum from the organism, and, at the same time, could prevent illness. This is all the more so

because no symptoms of a disease resembling podagra were observed in the regions of the other molybdenum provinces, Kadzharan and Dastakert, where, in addition to high molybdenum content, there is an even higher copper content.

All of this suggests that the existence of an endemic disease very similar in its primary symptoms to podagra is possible. Elevated synthesis of uric acid is, it would appear, mandatory if there is to be an increase in the xanthine oxidase activity, because the formation of uric acid always takes place at the stage where catalysis is by the xanthine oxidase, regardless of the path from the synthesis of the uric acid nucleus to the formation of hypoxanthine.

Xanthine oxidase is an enzyme that contains molybdenum, and its synthesis depends on the content of molybdenum in the organism, with this latter in turn dependent on the molybdenum contained in the environment. So far as we know, nothing has been published on xanthine oxidase activity as an etiological factor in podagra. Our data concerning the possibility of the participation of molybdenum in the etiology of podagra still point to one of the possible causes of the onset of this disease.

CONCLUSIONS

The regions in Armenia that were studied (Ankavan, Kadzharan, and Dastakert) are biogeochemical provinces infiltrated by molybdenum. The content of molybdenum in the soils, waters, and living organisms in these provinces exceed the usual concentration of this element in other regions.

The content of molybdenum in the soil depends on the infiltration by this element of the basement rock. Maximum quantities of molybdenum are found in slightly alkaline and neutral soils, as well as in soils the features of which are high contents of organic matter. It is in these soils that the molybdenum is most available for plants. The plant molybdenum concentration is determined by how much molybdenum there is in the environment, and by the status of the species, at the same time that the plant molybdenum content correlates in the majority of plants with the soil molybdenum content. Maximum quantities of molybdenum are stored by representatives of the legume, mint, figwort, and aster families, the least by the gramen.

Biochemical research resulted in findings of definite reactions on the part of animal organisms to an elevated content of molybdenum in the environment. The degree to which these reactions occur depends on the quantity of copper in the environment, with the effect of the molybdenum more striking for relatively less copper content.

Given the conditions that exist in molybdenum provinces, there is an increase in the xanthine oxidase activity in the tissues of animals, and something of an increase in the excretion of the daily quantity of uric acid. No increase in blood uric acid content was observed in animals.

An endemic disease that is similar in its symptoms to podagra develops in man within the limits of the Ankavan molybdenum province. The disease is accompanied by an increased blood molybdenum content, increased excretion from the organism of copper, increased xanthine oxidase activity,

and an increase in blood uric acid content. This is the basis for the assumption that an increase in the molybdenum content in the human body is one of the etiological factors for the podagra occurring among people who live under the conditions prevailing in a geochemical environment in which there is an elevated molybdenum content.

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